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Crystal and Molecular Structure of $(CO)_6Fe_2B_3H_7$, a Diiron Analogue of Pentaborane(9)

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The solid-state structure of $(CO)_6Fe_2B_3H_7$ consists of a B_3H_7 fragment bound to one iron of a "sawhorse" $Fe_2(CO)_6$ fragment through two Fe–H–B bridge hydrogen bonds and to the other iron through multicenter iron–boron bonding. The molecule has approximate C_s symmetry, one iron being six-coordinate (three carbonyl ligands, two Fe–H–B bridging hydrogens, and one iron) while the other iron is seven-coordinate (three carbonyl ligands, three borons, and one iron). Each boron atom has a single terminal hydrogen, and the other two hydrogens in the molecule bridge between the boron atoms. The simplest description of the molecular structure is as a derivative of B_5H_9 in which one apical and one basal BH group are replaced by $Fe(CO)_3$ groups. As such, this molecule constitutes another demonstration of the usefulness of the borane analogy. Crystals of $(CO)_6Fe_2B_3H_7$ form in the monoclinic space group $P2_1/c$ with unit cell parameters (at −20 °C) a = 9.006 (2) Å, b = 10.878 (2) Å, c = 12.479 (2) Å, β = 99.54 (1)°, V = 1206 Å^3, and Z = 4. The X-ray structure was solved as described in the text and refined to R = 0.055 and R_w = 0.059 for 3157 independent $[F_o \geq 3\sigma(F_o)]$ reflections.

Introduction

The structural relationship that has been shown to exist between borane cages and transition-metal clusters has been referred to as the "borane analogy".[1] The primary observable expression of the "borane analogy" is geometrical structure, i.e., in the association of $n + 1$ framework or cluster electron pairs with an n-atom deltahedral cluster structure. These electron counting rules are best applied to small, closed clusters composed of first row atoms and will not be obeyed in every instance. Examples of nonborane-like clusters have been well characterized.[2] On the other hand, the "borane analogy" does serve as a valid first-order model of cluster structure. By contrasting observed cluster structure and properties with this model, unique properties of the nonborane clusters are highlighted.

In this spirit, we have set out to compare the structure and properties of a homologous series of metalloboranes in which metal content is the variable. The five-atom system has been chosen as it is the smallest cluster that requires some measure of delocalized bonding and, hence, the smallest deserving of the name cluster. The series is $[(CO)_3Fe]_{5-n}B_nH_{n+4}$, the first two members of which are B_5H_9[3] and $B_4H_8Fe(CO)_3$[4] with structures indicated in Figure 1. Here we report the crystal and molecular structure of a third and new member of the series, $B_3H_7Fe_2(CO)_6$.[5]

Crystal Structure Determination

A single crystal of $B_3H_7Fe_2(CO)_6$,[5] 0.8 × 0.3 × 0.4 mm, was grown in a capillary by annealing a polycrystalline sample at 45 °C. Preliminary examination of the crystal on a Syntex P$\bar{1}$ diffractometer showed the crystal to be monoclinic. The systematic absences of $h0l$ when $l = 2n + 1$ and $0k0$ when $k = 2n + 1$ are unique for the space group $P2_1/c$ (No. 14). The unit cell parameters (at −20 ± 3 °C, λ(Mo K$\bar{\alpha}$) = 0.71073 Å) are a = 9.006 (2) Å, b = 10.878 (2) Å, c = 12.479 (2) Å, and β = 99.54 (1)°. These parameters were determined from a least-squares refinement utilizing the setting angles of 30 accurately centered reflections (30° < 2θ < 34°), each collected at $\pm 2\theta$. The unit cell volume of 1206 Å^3 led to a calculated density of 1.76 g/cm^3 for four molecules of $B_3H_7Fe_2(CO)_6$ per unit cell.

X-ray intensity data were collected on a Syntex P$\bar{1}$ diffractometer equipped with a graphite-monochromated Mo Kα radiation source using θ–2θ scans with a scan range from 2θ(Mo Kα_1) − 0.65° to 2θ(Mo Kα_2) + 0.65° (λ(Mo Kα_1) = 0.709 29 Å, λ(Mo Kα_2) = 0.713 59 Å). Variable scan rates (2–24°/min) were employed, and stationary-crystal, stationary-counter backgrounds were measured at both ends of the scan, each for one-fourth the time of the scan. Four standard reflections were measured every 50 reflections during data collection to monitor the long-term stability; no significant deviations were noted. The intensity data were reduced and standard deviations calculated as previously described.[6] The data with $F_o > 3\sigma(F_o)$ were retained as observed, leading to 3157 reflections (72% of the theoretical number possible for $(\sin\theta)/\lambda \leq 0.76$ Å^{-1}) that were used for the refinement of the structure. ψ scans showed intensity variations of ~40%, and absorption corrections were applied (empirical ψ scan method μ_{Mo} = 2.31 mm^{-1}).

The iron atoms and 10 of the light atoms were located by direct methods using the MULTAN package.[7] The rest of the nonhydrogen atoms were located by standard Fourier techniques. The model was refined to convergence on the assumption that the atoms vibrate anisotropically (only the first half of the data was utilized up to this point). The hydrogen atoms were located from a difference electron density map and included in the model as isotropic atoms.

Refinement of the complete structure was based on F_o. Atomic scattering factor curves for the nonhydrogen atoms were taken from the tabulation of Cromer and Waber,[8] and the curve for hydrogen

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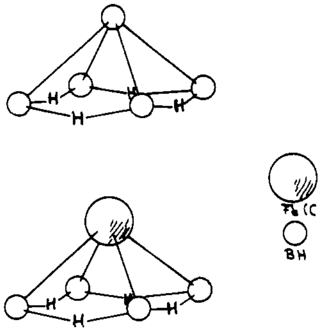

Figure 1. Structures of the first members of the five-atom nido-cage series $[(CO)_3Fe]_{5-n}B_nH_{n+4}$, B_5H_9, and $(CO)_3FeB_4H_8$.

Table I. Fractional Monoclinic Coordinates and Isotropic Temperature Factors in $B_3H_7Fe_2(CO)_6$[a]

atom	x	y	z	B,[b] Å^2
Fe_2	0.36159 (5)	0.95120 (4)	0.24185 (4)	2.8
Fe_1	0.11743 (5)	0.98693 (4)	0.31716 (3)	2.6
C_1	0.4202 (4)	0.8191 (4)	0.3237 (3)	3.9
C_2	0.4612 (4)	1.0536 (4)	0.3412 (3)	3.7
C_3	0.5040 (4)	0.9363 (4)	0.1547 (3)	3.9
C_4	0.1439 (4)	0.8569 (3)	0.40718 (28)	3.6
C_5	−0.0747 (4)	0.9989 (3)	0.32726 (28)	3.5
C_6	0.1746 (4)	1.1120 (4)	0.40932 (28)	3.5
O_1	0.4589 (4)	0.7343 (3)	0.37301 (27)	5.6
O_2	0.5238 (3)	1.1190 (3)	0.40289 (27)	5.2
O_3	0.5917 (3)	0.9256 (3)	0.10133 (28)	5.4
O_4	0.1568 (4)	0.7732 (3)	0.46158 (24)	5.1
O_5	−0.1997 (3)	1.0052 (3)	0.33414 (27)	4.9
O_6	0.2066 (4)	1.1929 (3)	0.46607 (25)	5.0
B_1	0.1828 (5)	1.0994 (4)	0.1992 (3)	3.4
B_2	0.0279 (5)	1.0003 (5)	0.1549 (3)	3.7
B_3	0.1333 (5)	0.8640 (4)	0.1932 (3)	3.4
H_1	0.302 (5)	1.062 (4)	0.167 (3)	4.4 (9)
H_2	0.263 (4)	0.860 (4)	0.150 (3)	4.7 (10)
H_3	0.098 (5)	1.072 (4)	0.107 (3)	4.8 (10)
H_4	0.054 (5)	0.911 (4)	0.098 (3)	5.3 (10)
H_5	0.184 (4)	1.190 (4)	0.206 (3)	4.1 (9)
H_6	−0.091 (5)	1.023 (4)	0.129 (4)	4.3 (9)
H_7	0.102 (5)	0.776 (5)	0.197 (4)	5.8 (11)

[a] The estimated standard deviations of the least significant digits are given in parentheses. [b] The isotropic equivalents are given for the atoms that were refined anisotropically.

was taken from Stewart, Davidson, and Simpson.[9] The effects of anomalous scattering for the iron atoms were included in the calculated structure factors.[10] The final values for the discrepancy indices were $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.055$ and $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} = 0.059$. The final data/parameter ratio was 17.3; the estimated standard deviation of an observation of unit weight was 1.79. The largest peak on the final difference electron density map was ~1 e/Å^3.

The final atomic coordinates and isotropic thermal parameters are given in Table I, selected interatomic distances and angles are given in Table II, root-mean-square amplitudes of vibration along the principal axes for the nonhydrogen atoms are given in Table III, and anisotropic thermal parameters are given in Table IV.

Description of the Structure

The static molecular structure of $(CO)_6Fe_2B_3H_7$ and the numbering system used are shown in Figures 2–4. Except for a small twist of the apical $Fe(CO)_3$ fragment (see below) the molecule possesses a plane of symmetry defined by Fe_1, Fe_2, and B_2. The molecule consists of a bent "sawhorse" $Fe_2(CO)_6$ fragment to which a triangular borane fragment is unsymmetrically bound such that the iron attached to the bridging hydrogens is six-coordinate with distorted octahedral geometry whereas the other iron is effectively seven-coordinate. Alternatively, the two irons and three borons define a distorted square-pyramidal cage in which the edges of the square base contain bridging hydrogens. As such the structure is analogous to that of pentaborane(9) in which an apical and a basal BH fragment are replaced by formally equivalent $Fe(CO)_3$ fragments. The major difference is that the basal iron atom lies 0.21 Å below the plane of the three borons and 0.62 Å further than B_2 from the $B_1Fe_1B_3$ plane.

The distances (Table II) in the borane fragment are normal.[11] Note that, as is the case with other boranes,[10] the BHB

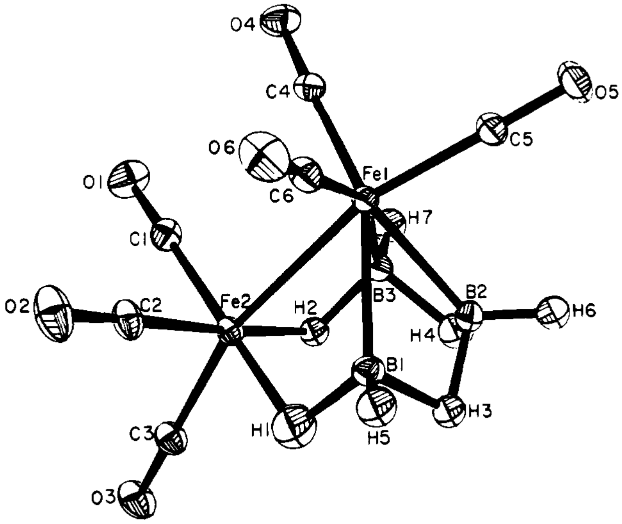

Figure 2. Static molecular structure of $(CO)_6Fe_2B_3H_7$. All atoms in this ORTEP diagram are represented by 50% thermal ellipsoids.

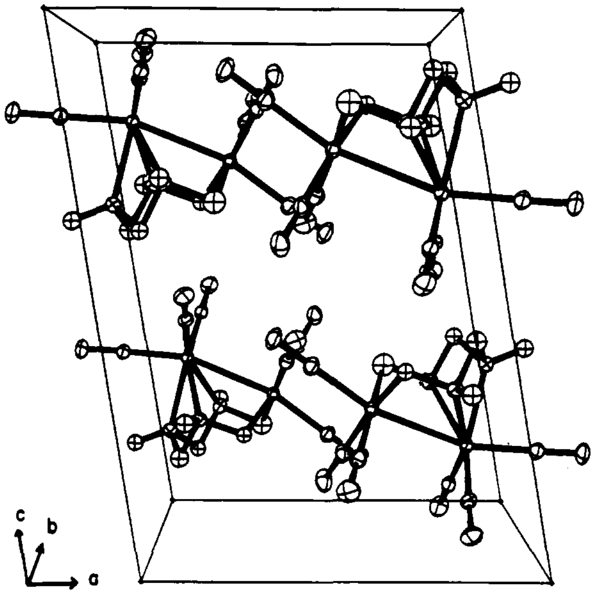

Figure 3. Packing diagram showing the contents of one unit cell projected on the *ac* plane.

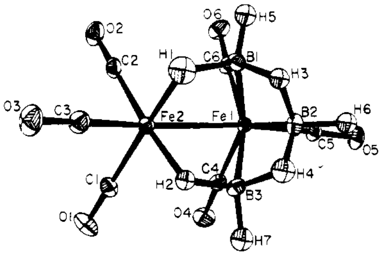

Figure 4. View of $(CO)_6Fe_2B_3H_7$ showing the small twist of the apical $Fe(CO)_3$ group around the pseudo-fourfold axis.

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Table II. Selected Interatomic Distances (Å) and Angles (Deg) for $B_3H_7Fe_2(CO)_6$[a]

Distances

Fe_1-Fe_2	2.559 (2)	Fe_1-B_3	2.065 (4)	B_1-H_1	1.27 (4)
Fe_2-B_1	2.275 (4)	Fe_1-C_4	1.794 (4)	B_1-B_5	0.99 (4)
Fe_2-B_2	3.068 (4)	Fe_1-C_5	1.759 (4)	B_1-H_3	1.30 (4)
Fe_2-B_3	2.251 (4)	Fe_1-C_6	1.798 (4)	B_2-B_3	1.780 (6)
Fe_2-H_1	1.56 (4)	C_1-O_1	1.129 (5)	B_2-H_3	1.22 (4)
Fe_2-H_2	1.66 (4)	C_2-O_2	1.126 (4)	B_2-H_4	1.24 (4)
Fe_2-C_1	1.788 (4)	C_3-O_3	1.120 (4)	B_2-H_6	1.10 (4)
Fe_2-C_2	1.789 (4)	C_4-O_4	1.129 (4)	B_3-H_2	1.37 (4)
Fe_2-C_3	1.820 (4)	C_5-O_5	1.144 (4)	B_3-H_4	1.38 (4)
Fe_1-B_1	2.070 (4)	C_6-O_6	1.134 (4)	B_3-H_7	1.00 (5)
Fe_1-B_2	2.054 (5)	B_1-B_2	1.774 (6)		
		B_1-B_3	2.599 (7)		

Angles

$Fe_1-Fe_2-C_1$	95.82 (13)	$B_3-Fe_1-C_6$	156.70 (16)
$Fe_1-Fe_2-C_2$	90.76 (13)	$C_4-Fe_1-C_5$	92.46 (18)
$Fe_1-Fe_2-C_3$	164.93 (13)	$C_4-Fe_1-C_6$	101.59 (18)
$Fe_1-Fe_2-H_1$	82.6 (15)	$C_5-Fe_1-C_6$	94.47 (17)
$Fe_1-Fe_2-H_2$	87.3 (13)	$Fe_2-C_1-O_1$	178.0 (4)
$C_1-Fe_2-C_2$	92.17 (19)	$Fe_2-C_2-O_2$	179.3 (4)
$C_1-Fe_2-C_3$	95.72 (18)	$Fe_2-C_3-O_3$	179.1 (4)
$C_1-Fe_2-H_1$	176.5 (15)	$Fe_1-C_4-O_4$	177.7 (3)
$C_1-Fe_2-H_2$	89.5 (14)	$Fe_1-C_5-O_5$	179.2 (4)
$C_2-Fe_2-C_3$	98.44 (18)	$Fe_1-C_6-O_6$	177.8 (4)
$C_2-Fe_2-H_1$	90.9 (15)	$Fe_1-B_1-H_1$	113.0 (19)
$C_2-Fe_2-H_2$	177.6 (14)	$Fe_1-B_1-H_3$	107.4 (19)
$C_3-Fe_2-H_1$	85.4 (15)	$Fe_1-B_1-H_5$	121.9 (23)
$C_3-Fe_2-H_2$	83.1 (13)	$H_1-B_1-H_3$	92.9 (24)
$H_1-Fe_2-H_2$	87.4 (21)	$H_1-B_1-H_5$	110.3 (29)
$Fe_2-Fe_1-B_1$	57.71 (12)	$H_3-B_1-H_5$	107.1 (29)
$Fe_2-Fe_1-B_2$	82.46 (15)	$Fe_1-B_2-H_3$	111.9 (20)
$Fe_2-Fe_1-B_3$	57.07 (12)	$Fe_1-B_2-H_4$	115.3 (20)
$Fe_2-Fe_1-C_4$	94.46 (13)	$Fe_1-B_2-H_6$	120.5 (24)
$Fe_2-Fe_1-C_5$	162.14 (12)	$H_3-B_2-H_4$	93.3 (28)
$Fe_2-Fe_1-C_6$	100.22 (12)	$H_3-B_2-H_6$	106 (3)
$B_1-Fe_1-B_2$	50.96 (18)	$H_4-B_2-H_6$	106.1 (29)
$B_1-Fe_1-B_3$	77.69 (18)	$Fe_1-B_3-H_2$	119.2 (17)
$B_1-Fe_1-C_4$	152.16 (16)	$Fe_1-B_3-H_4$	108.2 (19)
$B_1-Fe_1-C_5$	113.97 (17)	$Fe_1-B_3-H_7$	122.1 (25)
$B_1-Fe_1-C_6$	85.60 (18)	$H_2-B_3-H_4$	91.2 (23)
$B_2-Fe_1-B_3$	51.21 (19)	$H_2-B_3-H_7$	105 (3)
$B_2-Fe_1-C_4$	131.36 (19)	$H_4-B_3-H_7$	107 (3)
$B_2-Fe_1-C_5$	80.61 (18)	$Fe_2-H_1-B_1$	106.4 (26)
$B_2-Fe_1-C_6$	126.82 (19)	$Fe_2-H_2-B_2$	95.6 (22)
$B_3-Fe_1-C_4$	86.59 (18)	$B_1-H_3-B_2$	89.6 (27)
$B_3-Fe_1-C_5$	107.06 (17)	$B_2-H_4-B_3$	85.3 (25)
$B_1-B_2-B_3$	93.72 (27)	$Fe_2-B_3-B_2$	98.27 (24)
$B_1-Fe_2-B_3$	69.92 (16)	$B_3-H_2-Fe_2$	95.6 (22)
$Fe_2-B_1-B_2$	97.58 (25)		

[a] The estimated standard deviations of the least significant digits are given in parentheses.

Table III. Root-Mean-Square Amplitudes of Vibration (in Å) for $B_3H_7Fe_2(CO)_6$[a]

atom	min	intermed	max
Fe_2	0.1787 (6)	0.1833 (7)	0.2081 (6)
Fe_1	0.1724 (6)	0.1814 (6)	0.1899 (6)
C_1	0.196 (4)	0.225 (4)	0.249 (5)
C_2	0.181 (4)	0.215 (5)	0.261 (5)
C_3	0.199 (4)	0.217 (5)	0.257 (5)
C_4	0.195 (4)	0.216 (4)	0.226 (4)
C_5	0.189 (4)	0.213 (4)	0.229 (4)
C_6	0.196 (4)	0.203 (4)	0.235 (4)
O_1	0.195 (4)	0.278 (4)	0.343 (4)
O_2	0.196 (4)	0.235 (4)	0.362 (4)
O_3	0.192 (4)	0.276 (4)	0.334 (4)
O_4	0.192 (4)	0.288 (4)	0.297 (4)
O_5	0.186 (4)	0.264 (4)	0.317 (4)
O_6	0.189 (4)	0.261 (4)	0.321 (4)
B_1	0.186 (5)	0.207 (5)	0.230 (5)
B_2	0.177 (5)	0.219 (5)	0.259 (6)
B_3	0.178 (5)	0.213 (5)	0.232 (5)

[a] The estimated standard deviations of the least significant digits are given in parentheses.

bridges are unsymmetrical in this compound with both shorter BH distances associated with B_2. Table V compares selected distances and bond angles of other compounds that contain or can be considered to contain the B_3H_7 fragment. In a comparison of these molecules, the parameter exhibiting the largest change is the B_1-B_3 distance or, alternatively, the $B_1-B_2-B_3$ angle. Thus, the latter changes from 61° in $B_3H_8^-$[12] to 90° in B_5H_9[13] to 94° in $(CO)_6Fe_2B_3H_7$ to 113° in $L_2PtB_3H_7$.[14] Comparison of all the information in Table V shows a close correspondence between the structural parameters of B_3H_7 in $(CO)_6Fe_2B_3H_7$ and B_3H_7 in B_5H_9. Insofar as geometry reflects the nature of chemical bonding, there is a striking similarity between the bonding of B_3H_7 to B_2H_2 in B_5H_9 and the bonding of B_3H_7 to $Fe_2(CO)_6$ in $(CO)_6Fe_2B_3H_7$. Hence this compound provides another example of the borane analogy[1] in the sense that the easiest, useful description of the structure of $(CO)_6Fe_2B_3H_7$ is as a formal derivative of B_5H_9.

Table VI compares the structural parameters of the $Fe(CO)_3$ fragments in $(CO)_6Fe_2B_3H_7$ with average values of these parameters in other compounds containing the $Fe_2(CO)_6$ fragment. For both apical and basal iron fragments the Fe–C and C–O distances are very close to those found in other compounds. In addition all the Fe–C–O angles are close to 180°. Although the C–Fe–C angles for the basal $Fe(CO)_3$ fragment compare well with those for the other compounds,[15] there are some differences for the apical iron fragment. This is not surprising as here the apical iron is formally seven-coordinate. It should also be noted that there is a slight twist of the apical $Fe(CO)_3$ around the idealized fourfold axis of the square-pyramidal cage so that C_5 does not lie in the plane defined by Fe_1, Fe_2, and B_2 and the $Fe_2(CO)_6$ fragment does not quite have C_{2v} symmetry. (See Figure 4.)

The $(CO)_6Fe_2B_3H_7$ molecule contains two iron atoms with an Fe–Fe distance of 2.56 Å. This is very similar to the Fe–Fe distance in other compounds containing the $Fe_2(CO)_6$ fragment, e.g., $(CO)_6Fe_2S_2$ (2.55 Å),[16] but it must be kept in mind that the Fe–Fe distance can be strongly perturbed by changing the nature of the bridging ligand,[17] e.g., $(CO)_6Fe_2(CH_2S_2)$ (2.48 Å).[18] Bridged, diiron compounds such as $(CO)_6Fe_2S_2$ are considered to have a bent metal–metal bond in the sense that the Fe–C_{ax} bond vectors do not meet at θ = 180° (see I).[15] It is interesting to note that the Fe–Fe bond in $(CO)_6Fe_2B_3H_7$ is less bent (θ = 147°) than that in $(CO)_6Fe_2S_2$ (θ = 130°).[19] The final comparison is with $(CO)_{15}Fe_5C$,[20]

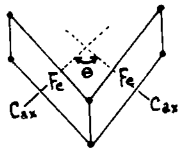

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Table IV. Anisotropic Thermal Parameters (Å^2) for $B_3H_7Fe_2(CO)_6$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe_2	2.574 (18)	3.022 (20)	3.004 (18)	0.095 (14)	0.423 (13)	−0.380 (14)
Fe_1	2.427 (16)	2.846 (19)	2.505 (16)	−0.074 (13)	0.301 (12)	−0.031 (13)
C_1	3.77 (15)	4.01 (16)	4.12 (16)	0.78 (13)	0.57 (12)	−0.33 (13)
C_2	2.70 (13)	4.41 (17)	4.51 (17)	0.36 (12)	0.50 (11)	−0.83 (14)
C_3	3.58 (15)	4.65 (18)	3.97 (16)	−0.08 (13)	0.96 (12)	−0.84 (14)
C_4	3.79 (15)	3.89 (16)	3.11 (13)	−0.19 (12)	0.67 (11)	0.19 (12)
C_5	3.63 (14)	4.01 (16)	2.93 (12)	−0.21 (12)	0.53 (10)	−0.37 (11)
C_6	3.16 (13)	3.90 (16)	3.66 (14)	−0.28 (11)	0.79 (11)	−0.51 (12)
O_1	7.40 (20)	5.00 (15)	6.05 (17)	2.87 (15)	1.13 (14)	0.94 (14)
O_2	3.84 (13)	6.76 (18)	7.01 (18)	−0.58 (12)	0.33 (12)	−3.45 (16)
O_3	4.12 (13)	7.87 (21)	6.30 (17)	−0.07 (13)	2.39 (12)	−1.47 (15)
O_4	6.97 (18)	4.87 (15)	4.66 (14)	0.04 (13)	1.04 (12)	1.79 (12)
O_5	2.89 (11)	7.86 (20)	5.61 (16)	0.09 (12)	1.13 (11)	−0.50 (14)
O_6	5.76 (15)	5.26 (16)	5.49 (15)	−1.23 (12)	1.30 (12)	−2.50 (13)
B_1	3.49 (16)	3.29 (16)	3.57 (16)	0.48 (13)	0.70 (12)	0.57 (13)
B_2	3.16 (15)	5.18 (22)	3.01 (15)	−0.13 (15)	−0.17 (12)	0.38 (15)
B_3	3.53 (16)	3.54 (17)	3.19 (15)	−0.68 (13)	0.33 (12)	−0.59 (13)

[a] The B_{ij}'s are related to the dimensionless β_{ij}'s employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j$. The estimated standard deviations of the least significant digits are given in parentheses.

Table V. Comparison of $(CO)_6Fe_2B_3H_7$ to Other Compounds Containing a B_3H_7 Fragment

	$(CO)_6Fe_2B_3H_7$[a]	B_5H_9[b]	$L_2PtB_3H_7$[c]	$B_3H_8^-$[d]
	Distances, Å			
B_1-B_2, B_2-B_3[e]	1.77, 1.78	1.77	1.86, 1.92	1.77
B_1-B_3	2.60	2.51	3.15	1.80
B-H_{term}	1.00–1.30	1.20		1.05–1.20
B-$H_{bridge\text{-}B}$	0.99–1.38	1.35	*f*	1.2–1.5
B-$H_{bridge\text{-}Fe}$	1.27–1.37		*f*	
	Angles, Deg			
B_1-B_2-B_3	93.7	90	112.9	61.1
B_1-H_3-B_2, B_2-H_4-B_3	89.6, 85.3	82	*f*	81
Fe_1-B_2-H_6	120.5	115	*f*	
H_3-B_2-H_4	93.3	92.6	*f*	145
H_1-B_1-H_3, H_2-B_3-H_4	92.9, 91.2		*f*	

[a] This work. [b] Reference 13. [c] Reference 14. [d] Reference 12. [e] Notation is for $(CO)_6Fe_2B_3H_7$. [f] Hydrogen atoms not located in this structure.

Table VI. Comparison of the Structural Parameters of the $Fe(CO)_3$ Fragments of $(CO)_6Fe_2B_3H_7$

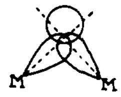
	dist, Å		angles, deg	
	Fe-C	C-O	C_{ax}-FeC_{eq}	C_{eq}-FeC_{eq}
$Fe(CO)_3$ basal	1.79	1.13	95.7	92.2
	1.79	1.13	98.4	
	1.82	1.12		
$Fe(CO)_3$ apical	1.79	1.13	94.5	101.6
	1.76	1.14	92.5	
	1.80	1.13		
av $Fe(CO)_3$[a]	1.77-1.81	1.14-1.17	97.5-100.2	88.7-95.3

[a] Reference 15.

a molecule that, as a cage, is formally related to $(CO)_6Fe_2B_3H_7$.[1] In the carbide cluster the average of the apical–basal iron–iron distances is 2.62 Å while the basal–basal iron–iron average distance is 2.66 Å. Both are longer than the iron–iron distance in $(CO)_6Fe_2B_3H_7$.

As the structures of transition-metal hydride complexes are of current interest,[21] the structural features of the two B–H–Fe interactions in $(CO)_6Fe_2B_3H_7$ deserve comment. The B–H–B bond in B_5H_9 is considered an "open" bond (II)[3] while the M–H–M bond in $HW_2(CO)_9NO$ is considered "closed" (III) with some direct metal–metal interaction.[21] The evidence used

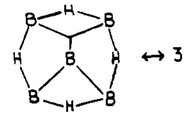
II



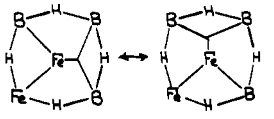
III

to decide the latter case was the fact that in the compound cited the bridging hydrogen does not lie at the intersection of the two axial metal–ligand vectors as would be expected if there were not direct metal–metal interactions. The situation of the two B–H–Fe interactions in $(CO)_6Fe_2B_3H_7$ is as follows. The average C–Fe_2–H angle is 177° where C is trans to the B–H–Fe bridging hydrogen. The boron atoms are expected to be tetrahedral,[3] and the average angles between the Fe–H–B bridging hydrogens and the other three ligands attached to the pair of Fe–H–B borons are 116, 92, and 108° with a net average value of 105°. Thus, these data provide no evidence for direct metal–boron interaction, and the Fe–H–B bond is considered an "open" three-center bond analogous to B–H–B.[22] The Fe_2–H bridge distances are similar to those found in $(CO)_3FeB_5H_8^-$ and $[Cu[P(C_6H_5)_3]_2][B_5H_8Fe(CO)_3]$.[23]

As pointed out above $(CO)_6Fe_2B_3H_7$ is a structural analogue of B_5H_9, suggesting a valence-bond representation of the electronic structure of the ferraborane similar to that for B_5H_9. In terms of two-center BB bonds, open three-center BHB bonds, and closed three-center BBB bonds the cage bonding in B_5H_9 is expressed by IV plus the three equivalent resonance



IV



V

structures. For $(CO)_6Fe_2B_3H_7$ the addition of three-center BHFe and two-center FeFe bonds allows the description given in V. In this description the total contribution of each $Fe(CO)_3$ fragment and BH fragment to the cage bonding is two electrons and three orbitals. Such a representation permits only two resonance structures and would suggest a lower net bond

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(20) Braye, E. H.; Dahl, L. F.; Hübel, W.; Wampler, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 4633.

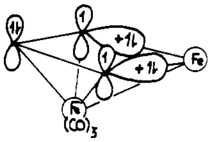
(21) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

(22) This argument is weakened by the fact that the bond angles used are taken from bonds containing hydrogen nuclei which are not well located by the X-ray method.

(23) Fehlner, T. P.; Ragaini, J.; Mangion, M.; Shore, S. G. *J. Am. Chem. Soc.* **1976**, *98*, 7085. Mangion, M.; Ragaini, J.; Schmitkons, T. A.; Shore, S. G. *Ibid.* **1979**, *101*, 754.

order between the apical iron and B_2 compared to B_1 and B_3. Within experimental error the apical iron–basal boron bond distances are equal (Table II) which means either that the bonding description is oversimplified or that intracage distances are not very sensitive to net bond order.[24] Other differences in bonding between B_5H_9 and $(CO)_6Fe_2B_3H_7$ are expected when compared in detail; however, the qualitative similarities presented here are fully supported by the observed geometrical structure. Hence, the ferraborane may be usefully described as a nido ($n + 2 = 7$ electron pairs) cage or cluster.

An alternative description of the bonding results if one investigates the effective atomic number, EAN, of each iron atom. The $(CO)_6Fe_2B_3H_7$ molecule can be formally considered as formed by the addition of $B_3H_7^{2-}$ to $Fe_2(CO)_6^{2+}$ as depicted in VI. In this view the π system of the borallyl ion donates four electrons to one iron while the two BH bonds donate four electrons to the other iron.[25] Hence, as each iron is d^7, has three CO ligands, and shares an Fe–Fe bond, the 18-electron rule is satisfied. However, as pointed out above, the geometry of B_3H_7 in $(CO)_6Fe_2B_3H_7$ is substantially different from that of the B_3 unit in the structurally characterized borallyl complex $L_2PtB_3H_7$.[14] The organometallic description may be formally correct, but the cage description of the bonding is more realistic in terms of geometry.[26]



VI

Acknowledgment. The aid of Professor W. R. Scheidt as well as the support of the National Science Foundation under Grant CHE 78-11600 is gratefully acknowledged.

Registry No. $(CO)_6Fe_2B_3H_7$, 71271-99-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[24] Extended Hückel calculations on this molecule also suggest a significant difference in bond order.[19]

[25] There are precedents for considering the Fe–H–B as a two-electron donor to the metal. See, for example: Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80.

[26] There is a similarity between the ferraborane and ferracyclopenadiene complexes. The latter complexes have a semi-bridging carbonyl primarily attached to the apical iron. With Cotton's method of electron counting, there is no need to invoke a semi-bridging carbonyl in the case of $(CO)_6Fe_2B_3H_7$ and indeed none is found: Cotton F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

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Crystal and Molecular Structure of the 1:2 Charge-Transfer Salt of Trimethyleneferrocene and 7,7,8,8-Tetracyano-*p*-quinodimethane: $[Fe(C_5H_4)_2(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$[1]

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The charge-transfer reaction between trimethyleneferrocene ($Fc(CH_2)_3$) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) results in a 1:2 salt of composition $[Fe(C_5H_4)_2(CH_2)_3{}^{+}\cdot][(TCNQ)_2{}^{-}\cdot]$. The crystal and molecular structures of this substance have been determined by single-crystal X-ray diffraction. The complex crystallizes as block plates in the centrosymmetric space group $C2/c$ with the unit cell constants of $a = 13.608$ (1) Å, $b = 7.738$ (1) Å, $c = 28.788$ (3) Å, $\beta = 94.336$ (8)°, $V = 3022.66$ Å^3, and $Z = 4$. The structure was solved by a combination of direct methods, Fourier, and full-matrix least-squares refinement techniques. A final $R_F = 0.049$ was obtained for 2328 reflections where $F_o^2 > \sigma(F_o^2)$. The structure consists of segregated stacks of $[(TCNQ)_2{}^{-}\cdot]$ dimers and trimethyleneferrocenium $[Fc(CH_2)_3{}^{+}\cdot]$ ions, respectively. The stacking distance between the $TCNQ^{1/2-}$ planes of each dimer is 3.162 (5) Å, while the distance between dimers is 3.423 (10) Å. The $[(TCNQ)_2{}^{-}\cdot]$ dimers form stacks which are inclined along the b axis, while the $[Fc(CH_2)_3{}^{+}\cdot]$ ions are aligned along the a axis and rotated 45° about the b axis. The sterically hindering trimethylene bridge causes the C_5 planes of the $[Fc(CH_2)_3{}^{+}\cdot]$ ion to be tilted at an angle of 13.7 (9)° with respect to each other. This amount is significantly greater than the ring tilt observed for other nonoxidized ferrocenes containing three-membered bridges. The bridging carbon atoms between the rings exhibit disorder. The bond distances of the exocyclic carbon–carbon bonds of the $[(TCNQ)_2{}^{-}\cdot]$ ion are 1.390 (3) and 1.394 (4) Å, which are consistent with a charge transfer of 0.5 e/TCNQ.

Introduction

We have undertaken a study of the charge-transfer reactions between metallocenes (principally substituted ferrocenes) and organic electron-accepting bases (principally 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and 2,3-dichloro-5,6-dicyanoquinone (DDQ)). Such charge-transfer complexes should be sublimable and, thus, permit the wide variety of physical studies that have been undertaken for (TTF)(TCNQ) (TTF = tetrathiafulvalene) to be extended to these materials. We have observed several unique and unusual materials: (1) 1:1 $[Fe(C_5(CH_3)_5)_2{}^{+}\cdot][TCNQ^{-}\cdot]$, a metamagnetic material with alternating ions along a stack,[3,4] (b) 1:1 $[Fe(C_5(CH_3)_5)_2{}^{+}\cdot]_2[(TCNQ)_2{}^{2-}]$, a paramagnetic dimeric material,[5,6]

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(2) (a) Argonne National Laboratory. (b) Undergraduate research participant from Luther College, Decorah, IA. (c) Occidental Research Corporation.

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